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W-2000 Hamburg 52(DE)(54) SiO₂-Flattening agent, process for its production and its use.

(57) A universally applicable SiO₂-flattening agent is described, which consists of SiO₂, 1 to 25 % by weight polyol and optionally 1 to 25 % by weight wax. The novel flattening agent is, even after lengthy storage, especially at pressure, still easily dispersible, does not lead to the formation of a hard sediment with non-thixotropic paints and lacquers, and has practically no negative effect on the thixotropic behaviour of paints and lacquers based on thixotropic polyamide-modified alkyd resins. The SiO₂, polyol and wax can be brought together in a variety of ways, e.g. during the micronization of the SiO₂ in a jet-mill or mechanical mill by adding polyol and wax at the same time, by spray-drying a suspension of SiO₂ in an aqueous polyol solution or even before drying by adding polyol during washing or an earlier production step. It is also possible to spray-dry a suspension of SiO₂, wax emulsion and polyol.

SiO₂ usual particle size
examples: 5 µ + 1.75 ml/g
1-25% wax [Appl. 15-30%]

pore volume
1.75 ml/g ex. 1
[Appl. 0.8 - 1.4)

FIELD OF THE INVENTION

The invention relates to a universally applicable SiO_2 -flatting agent, a process for its production and its use in thixotropic and non-thixotropic paints and lacquers.

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BACKGROUND OF THE INVENTION

The problem with thixotropic paints and lacquers based on polyamide-modified alkyd resins (see e.g. U.S. patent 2 663 649) is that the components additionally present in the lacquer, particularly hydroxyl group-containing solvents such as, for example, alcohols, glycols and some organic paint pigments (e.g. phthalocyanine blue, Hansa yellow and Bordeaux red), have a negative effect on the thixotropy. However, SiO_2 -flatting agents also have a similar effect.

Immediately after being produced, fine-particled SiO_2 -flatting agents can be easily de-agglomerated into individual particles with the application of low shearing forces when incorporated into lacquer. This behaviour is desirable because remaining agglomerates lead to clearly visible specks in the applied lacquer film. However, if fine-particled SiO_2 -flatting agents are subjected to a pressure, more solid agglomeration can result. This effect is increased if the pressure is exerted over a lengthy period of time. This can cause the good dispersibility of a product which initially has excellent dispersibility, to deteriorate during storage because of stress such as can occur during storage and transportation, whereupon said product is judged unacceptable by the user.

In thixotropic paints and lacquers, because of their gel-like properties, no sedimentation of flatting agents or pigment particles is observed. The particles remain in their position and cannot form a hard, non-dispersible sediment during storage. Exposure to shearing forces causes the viscosity of the system to fall substantially and the particles begin to settle. The particular feature of a thixotropic paint is that the viscosity is very rapidly restored as soon as the mechanical stress ceases. After a short time the paint once again has its original gel-like consistency, which prevents a further settling of the particles.

In a non-thixotropic paint, however, the situation is completely different, because here the SiO_2 -flatting agent particles settle and form a hard sediment. It is very difficult, and in many cases impossible, to re-disperse this sediment into the individual particles again with the equipment common in the paint and lacquer industry.

The formation of a hard sediment can be prevented by coating the flatting agent particles with wax. DE-PS 1 006 100 and DE-AS 1 592 865 describe how the SiO_2 -flatting agent particles can be coated with wax and which waxes can be used.

35 OBJECTS OF THE INVENTION

Therefore it is an object of the invention to provide a SiO_2 -flatting agent with the least possible negative effect or without any negative effect on the thixotropic behaviour of un-flatted thixotropic paints and lacquers based on polyamide-modified alkyd resins.

40 It is a further object of the invention to provide a SiO_2 -flatting agent which still has good dispersibility even after lengthy storage, particularly under pressure.

It is also an object of the invention to provide a SiO_2 -flatting agent which does not lead to the formation of a hard sediment with non-thixotropic paints and lacquers.

It is an additional object of the invention to provide a SiO_2 -flatting agent which is universally applicable.

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SUMMARY OF THE INVENTION

The invention is directed to a SiO_2 -flatting agent which is characterized in that it consists of SiO_2 and 1 to 25% by weight polyol. Preferably said SiO_2 -flatting agent additionally contains 1 to 25% by weight wax.

50 A further subject of the invention is a process for the production of a SiO_2 -flatting agent which is characterized in that SiO_2 is brought together with such an amount of polyol that the polyol content of the finished flatting agent is from 1 to 25% by weight. Preferably also such amount of wax is added that the wax content of the finished flatting agent is from 1 to 25% by weight.

Another subject of the invention is the use of the SiO_2 -flatting agent according to the invention for the production of thixotropic and non-thixotropic paints and lacquers.

Preferred embodiments and advantages of the invention will become apparent from the following detailed description of the invention and the subclaims.

DETAILED DESCRIPTION OF THE INVENTION

It was surprisingly found that the negative effect of SiO₂-based flattening agents on the thixotropy of paints and lacquers based on thixotropic polyamide-modified alkyd resins can be greatly reduced, or 5 eliminated, by the co-use of polyhydric alcohols. The affinity between the SiO₂ surface and the polyol is so great that even when the SiO₂ and the polyol are added separately to thixotropic paints and lacquers based on alkyd resins the polyol molecules are adsorbed by the SiO₂ surface. In other words, the modification according to the invention of SiO₂-flattening agents consists in impregnating or coating the SiO₂ surface with polyols. The realization that polyols eliminate the negative effect of the hydroxyl groups on the SiO₂ surface 10 is particularly surprising because alcohols and glycols in particular are known as substances which greatly impair the thixotropy of polyamide-modified alkyd resins. For example, a manufacturer of thixotropic polyamide-modified alkyd resins expressly points out that hydroxyl groups, as present in alcohols and glycols, completely destroy the thixotropic structure.

It was further surprisingly found that the good dispersibility of the fine-particle SiO₂-flattening agents 15 remains even during storage, and particularly during storage under pressure, if the SiO₂ surface is impregnated with a polyol.

Finally, it was surprisingly found that the impregnation or coating of the SiO₂-flattening agent surface with 20 polyols according to the invention is effective not only with pure but also with wax-coated flattening agents. This means, in other words, that the polyol applied according to the invention does not impair the effectiveness of the wax in terms of preventing the flattening-agent particles from settling and forming a hard sediment. Vice versa, the wax obviously does not have a negative effect on the thixotropy of thixotropic paints and lacquers, or on the improvement in dispersibility of SiO₂-flattening agents that can be achieved by 25 polyol impregnation after lengthy storage. The preferred SiO₂-flattening agent according to the invention can thus be applied universally not only in thixotropic but also in non-thixotropic paints and lacquers.

Alcohols of higher valence are suitable for the treatment of the SiO₂ surface according to the invention, particularly di- to hexahydric alcohols with, e.g., 2 to 100 carbon atoms, in which the carbon chains can be linear or branched and can be interrupted by any number of oxygen atoms (C-O-C groups = ethers). The OH-groups can be situated at any position. Mixtures of the named polyols can, of course, also be used.

Examples of polyols which are suitable according to the invention include glycerin, ethylene glycol, 30 diethylene glycol, polyethylene glycols, sorbitol, trimethylolpropane, di- trimethylolpropane, ethoxylated trimethylolpropanes, pentaerythritol and ethoxylated pentaerythritols.

With reference to waxes suitable according to the invention, reference is made to the aforementioned DE-PS 1 006 100 and DE-AS 1 592 865. Microcrystalline hard waxes, polyethylene waxes and partially oxidized polyethylene waxes, which have proved to be well suited, are mentioned in particular.

SiO₂-flattening agents are in most cases silica gels or precipitated silicic acids (also called precipitated silica). Pyrogenic silicic acids (or pyrogenic silicas) in the usual form are not used as flattening agents; there is, however, a form produced by secondary agglomeration which is likewise used as a flattening agent. Suitable are also dialytic silicic acids (or dialytic silicas). The particle size and particle-size distribution of the SiO₂-flattening agent lie within the usual ranges known to the expert.

The flattening agent according to the invention is prepared by bringing together SiO₂ with polyol and optionally wax. This is preferably done by micronizing the SiO₂ in a jet-mill or a mechanical mill, followed where appropriate by classification, and adding the polyol and optionally the wax (in melted form or as a powder) at the same time as the SiO₂. Another possibility is to spray-dry a suspension of SiO₂ in an aqueous polyol solution, to impregnate the resulting polyol-impregnated SiO₂, if desired, in the conventional manner with wax (see e.g. DE-PS 1 006 100 and DE-AS 1 592 865), and to adjust the SiO₂, now 40 impregnated with polyol and optionally wax, to the suitable particle-size distribution by air-classification or jet-milling. Alternatively, a suspension of SiO₂, wax emulsion and polyol can be spray-dried. The SiO₂ can also already be impregnated with polyol before drying by introducing polyol into the liquid phase surrounding the hydrogel or by adding polyol to the wash-water during washing (e.g. of the hydrogel in the case of silica gel) or impregnating the SiO₂ even earlier in the hydrosol state, by adding the polyol to the water glass or to the diluted sulphuric acid during the precipitation of the SiO₂. The polyol-treated SiO₂ 45 which is obtained according to one of these methods can then be impregnated with wax as described previously and adjusted to the suitable particle size distribution.

Alternatively, SiO₂ or wax-impregnated SiO₂ and polyol can be incorporated into the paint or lacquer as 50 separate components.

The advantageous effect of the modification of SiO₂-flattening agents with polyols according to the invention is probably due to the fact that the OH-groups of the SiO₂ surface are masked by addition and bonding via hydrogen-bridge bonds. It is decisive here for several OH-groups or ether groups to be present

per molecule to surpass the necessary adhesion vis-a-vis other polar molecules, e.g. water. Compared with the known esterification of OH groups on SiO₂ surfaces with alcohols, which is connected with a distinct enthalpy change, the difference according to the invention is that the modification of SiO₂-flatting agents with polyols takes place spontaneously but without noticeable enthalpy change. Accordingly, the production of the SiO₂-flatting agent according to the invention or the modification with polyol takes place basically below the temperature at which an esterification would take place, i.e. generally below 150 °C, preferably below 100 °C and especially at ambient temperature or an only slightly higher temperature.

Generally, 1 to 25% by weight polyol and in addition preferably 1 to 25% by weight wax, both relative to the weight of the SiO₂-flatting agent, are required for the modification of SiO₂-flatting agents according to the invention. Amounts of 3 to 15% by weight polyol and 3 to 10% by weight wax are preferred.

Practice of the invention will become further apparent from the following non-limiting examples.

Example 1 a

A SiO₂-flatting agent with an average particle size of 5 µm (measured with a Coulter Counter), a BET surface of 400 m²/g and a pore volume (both determined by nitrogen adsorption) of 1.75 ml/g was dispersed using a so-called dissolver (a high-speed stirring device with high shearing forces frequently used in the paint and lacquer industry for the dispersion of pigments and fillers) into a thixotropic lacquer containing a polyamide-modified thixotropic alkyd resin as its main component. The composition of the lacquer is given in the following table. The concentration of the flatting agent, relative to the solids content of the lacquer, was 9% by weight. The flattened lacquer was stored for 24 hours at 20 °C and then the viscosity was determined with the Haake viscosimeter (Haake RV3 Rotovisko, measuring head 500, spindle MV1). The measurement was carried out at 20 °C. A flow curve was determined from 0 to 32 rpm with a rotation-frequency change of 25 rpm/min/min. The viscosity was read off at 8 rpm from the curve with an increasing frequency of rotation. The results obtained are reproduced in Table 1.

Lacquer composition

		<u>parts by weight</u>
	Polyamide-modified thixotropic	
	alkyd resin, 50 %	70
35	urethane alkyd resin, 55 %	18.2
	barium-, cobalt- and lead octoate ¹⁾	2.1
	wetting agent	0.4
	de-foamer	0.2
40	levelling agent	0.5
	anti-skin agent	0.8
	white spirit K30	7.8
45		-----
		100.00

¹⁾ catalysts for drying by oxidation

50 After six weeks storage of the lacquer at room temperature no sediment was observed.

Example 1b

The SiO₂-flatting agent from Example 1a was impregnated with a wax by adding the wax into the jet mill at the same time as the SiO₂. The thus impregnated flatting agent, containing 10% by weight wax, was incorporated into the same lacquer as in Example 1a and tested as described there. The results are likewise reproduced in Table 1.

Example 2

The lacquer used in Example 1a was treated as in Example 1, but without the addition of a flattening agent. The corresponding tests were carried out with this lacquer and the results are likewise reproduced in 5 Table 1.

Example 3

10 The SiO₂-flattening agent used in Example 1a was already impregnated with a polyethylene glycol (molecular weight 400) during the micronization in the jet-mill, the polyethylene glycol being added into the jet-mill at the same time as the SiO₂. The polyethylene glycol concentration in the flattening agent was 8.5% by weight. The thus impregnated flattening agent was incorporated into the same lacquer as in Example 1a and tested as described there. The concentration of the flattening agent, relative to the solids content of the lacquer, was 9% by weight. The results are again reproduced in Table 1.

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Example 4 a

20 The SiO₂-flattening agent used in Example 1a was introduced into a non-thixotropic lacquer based on a nitrocellulose resin. The composition of the lacquer is given in the following table. The lacquer containing the flattening agent was kept for 6 weeks in a glass cylinder before the hardness of a sediment which may have formed was evaluated. The hardness was determined with a glass rod. The resistance felt on moving the sediment is the subjective criterion for evaluating the hardness.

The untreated flattening agent used in this example did form a hard sediment.

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Lacquer composition

	<u>parts by weight</u>
30 Nitrocellulose chips	12.6
toluene	30.0
butanol	5.6
35 ethyl acetate	6.0
methyl isobutyl ketone	20.0
plasticizer	2.3
silicone oil	1.0
40 alkyd resin/60% in xylene	22.5

	100.00

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Example 4b

50 Instead of the non-coated flattening agent from Example 1a, the wax-impregnated flattening agent from Example 1b was tested in the manner described in Example 4a with reference to sedimentation behaviour. In contrast to Example 4a, the wax-impregnated flattening agent led to a very soft and easily redispersible deposit.

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Example 5

Instead of the non-coated flattening agent from Example 1a, the polyol-impregnated flattening agent according to Example 3 was tested with reference to sedimentation behaviour as described in Example 4a. The SiO₂-flattening agent impregnated with 8.5% by weight polyethylene glycol led to the formation of a hard

deposit.

Example 6

5 The SiO₂-flatting agent used in Example 1a was already impregnated with a polyethylene glycol (molecular weight 400) and a wax during the micronization in the jet-mill, polyethylene glycol and wax being fed into the jet-mill at the same time as the SiO₂. The polyethylene glycol concentration in the flatting agent was 7.5% by weight and the wax concentration was 4% by weight. The impregnated flatting agent was incorporated into

10 a) the same lacquer as in Example 1a and
 b) the same lacquer as in Example 4a.

The results obtained with these lacquers are likewise given in Table 1.

The flatting agent of this Example led to the formation of a voluminous, very soft and easily redispersible sediment.

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Example 7

The polyethylene glycol in Example 6 was replaced by a polyol with 4 OH-groups and a molecular weight of 270. The impregnated flatting agent was again incorporated into

20 a) the same lacquer as in Example 1a and
 b) the same lacquer as in Example 4a.

The results obtained here are also reproduced in Table 1.

The flatting agent of this Example brought about the formation of a voluminous, very soft and easily redispersible sediment.

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Example 8a

The SiO₂-flatting agent according to Example 3 was incorporated into a non-thixotropic lacquer based on a polyurethane resin. The lacquer composition is reproduced in the following table. It is a representative example for lacquers commonly on the market. The sedimentation behaviour was tested as in Example 4a. The flatting agent treated with polyethylene glycol led to the formation of a hard sediment.

Lacquer composition

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	<u>parts by weight</u>
Urethane-alkyd resin, 55 % in white spirit	91.3
turpentine	1.0
40 white spirit	4.0
lead-drying agent	0.83
cobalt-drying agent	0.33
45 calcium-drying agent	1.27
anti-skin agent	1.27

	100.00

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Example 8b

55 Instead of the flatting agent according to Example 3, the flatting agent from Example 1b was tested as described in Example 8a. The formation of a very soft sediment, which was very easily redispersible, was observed.

Example 9

In this example the SiO_2 -flatting agent impregnated with polyethylene glycol and wax was incorporated into the lacquer described in Example 8a and tested in the same manner. This flatting agent led to the formation of a voluminous, very soft and easily redispersible sediment.

Table 1

Example	Flatting agent composition	Flatting agent concentration in lacquer	Lacquer composition according to example	Viscosity (mPa.s)	Sediment after six weeks' storage
1a	SiO_2 + Wax	9	1a	1405	no sediment
1b	SiO_2 + Wax	9	1a	1300	no sediment
2	no flatting agent	0	1a	3795	-
3	SiO_2 + PEG	9	1a	3950	no sediment
4a	SiO_2 + Wax	5	4a	-	hard sediment
4b	SiO_2 + Wax	5	4a	-	very soft sediment
5	SiO_2 + PEG	5	4a	-	hard sediment
6	SiO_2 + PEG + Wax	5	a) b)	3810	no sediment very soft deposit
7	SiO_2 + Polyol + Wax	5	a) b)	3690	no sediment very soft sediment
8a	SiO_2 + PEG	7	8a	-	hard sediment
8b	SiO_2 + Wax	7	8a	-	very soft sediment
9	SiO_2 + PEG + Wax	7	8a	-	very soft sediment

PEG : polyethylene glycol
 Polyol: polyol with 4 OH groups and a molecular weight of 270
 - : not measured

Example 10

Various flattening agents with two different particle sizes were prepared in the manner described in the foregoing examples. The composition of the flattening agents in each case is given in Table 2. Several bags of
5 the test products were stored together with untreated standard flattening agents for 6 weeks on palettes. Storage was carried out once with and once without an additional load of 200 kg/palette.

After the six weeks storage, 3 samples were taken from different bags. The dispersibility was evaluated according to the standard dispersion test described below. All samples were coded so that the testers were unable to identify the samples. The results are likewise reproduced in Table 2. The effectiveness of the
10 polyol impregnation is especially noticeable for the samples which were previously subjected to a load. Moreover, the test results show that the simultaneous impregnation with wax does not have a negative influence on the positive effect achieved by impregnation with polyol.

Standard Dispersion Test

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Testing was carried out on the lacquer described according to Example 4a.

Before use, the lacquer is set with MIBK to an outflow time of 70-85 seconds (beaker 4mm orifice/DIN 53211). 1.5 g flattening agent per 80 g lacquer are shaken with a Red Devil Paint Shaker for 40 seconds in a plastic beaker (diameter 6.5 cm, height 7.0 cm, 190 ml). After deaeration, the samples are briefly agitated
20 once more and drawn on to control cards using a 150 µm drawing spiral under dust-free conditions.

After 10 minutes the control cards are graded against standard cards. Rating 1 signifies that the lacquer coating is completely free of specks. The scale extends to 5. Rating 5 characterizes a lacquer coating with very many specks.

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Table 2

Sample	Flattening agent composition	Particle size (μm) (2)	Carbon content (%)	Dispersibility* after 6 weeks' storage with a load per palette of 0 kg 200 kg
1	100% SiO_2	3.4	0	1.2 3.9
2	90% SiO_2 , 10% PEG ⁽¹⁾	3.5	6.8	1.3 2.5
3	100% SiO_2 ,	5.3	0	1.4 3.1
4	90% SiO_2 , 10% PEG ⁽¹⁾	5.2	7.5	1.0 1.8
5	90% SiO_2 , 10% Wax	5.2	8.3	1.2 2.8
6	80% SiO_2 , 9% Wax, 11% PEG ⁽¹⁾	5.3	14.2	1.0 1.5

*measured according to the afore-mentioned Standard Dispersion Test; rating 1 = very good;
 5 = very bad
 (1) polyethylene glycol molecular weight 400
 (2) measured with the Coulter Counter

55 Example 11

The SiO_2 flattening agent used in Example 1a was already impregnated with glycerin during the micronization in the jet-mill by adding glycerin into the jet-mill at the same time as the SiO_2 . The glycerin

concentration in the flattening agent was 11% by weight. The thus impregnated flattening agent was incorporated into the same lacquer as in Example 1a and tested as described there. The results are reproduced in Table 3.

5 Example 12

10 Example 11 was repeated but with the addition of a polyol with 4 OH-groups and a molecular weight of 270 instead of glycerin during the micronization in the jet-mill. The polyol-concentration in the flattening agent was 12.5% by weight. The mixture was incorporated into the lacquer and tested as in Example 1a. The results are reproduced in Table 3.

Example 13

15 Example 1a was repeated but with a polyol with 4 OH-groups and a molecular weight of 270 in a concentration of 1.1% by weight added in dispersion at the same time as 7.9% by weight of SiO₂. The results of the tests are again reproduced in Table 3.

Example 14

20 Example 13 was repeated but, instead of the polyol with 4 OH-groups, a polyethylene glycol (molecular weight 400) was used. The concentration of the flattening agent, referred to the solids content of the lacquer, was 9% by weight (8.3% by weight SiO₂ + 0.7% by weight polyethylene glycol). The test results are also reproduced in Table 3.

25 Table 3

	Example No.	Flatting-agent concentration (% by weight)	Viscosity (mPa.s)
30	1a	9	1405
40	2	0	3795
	3	9	3950
	11	9	3715
45	12	9	3880
	13	9	4125
50	14	9	3950

The thorough testing of the lacquers in Examples 1a, 2, 3, and 11 to 14 produced no disadvantageous results as regards delay in drying, the dispersion state of the flattening agent and transparency.

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Claims

1. A SiO₂-flattening agent, characterized in that it consists of SiO₂ and 1 to 25% by weight polyol.

2. A flattening agent according to claim 1, which further consists of 1 to 25% by weight wax.
3. A flattening agent according to claim 1 or 2, which contains 3 to 15% by weight polyol.
5. 4. A flattening agent according to claim 2 or 3, which contains 3 to 10% by weight wax.
5. A flattening agent according to any preceding claim, in which the SiO₂ is silica gel, precipitated silicic acid, pyrogenic or dialytic silicic acid.
10. 6. Process for the production of a SiO₂-flattening agent, characterized in that SiO₂ is brought together with such an amount of polyol that the polyol content of the finished flattening agent is 1 to 25% by weight.
15. 7. Process according to claim 6 wherein SiO₂ is brought together with such an amount of polyol and wax that the polyol content of the finished flattening agent is 1 to 25% by weight and the wax content is 1 to 25% by weight.
8. Process according to claim 6 or 7 wherein such an amount of polyol is used that the polyol content of the finished flattening agent is 3 to 15% by weight.
20. 9. Process according to claim 7 or 8 wherein such an amount of wax is used that the wax content of the finished flattening agent is 3 to 10% by weight.
10. Process according to any of claims 6 to 9 wherein silica gel, precipitated silicic acid, pyrogenic or dialytic silicic acid is used as SiO₂.
25. 11. Process according to any of claims 6 to 10 wherein the SiO₂ is micronized in a jet-mill or mechanical mill, if need be with consequent classification, and polyol or polyol and wax are added at the same time as the SiO₂.
30. 12. Process according to claim 6 wherein a suspension of SiO₂ in an aqueous polyol solution is spray-dried, and the resulting SiO₂, which is impregnated with polyol, is adjusted by classification or jet-milling to the suitable particle-size distribution.
35. 13. Process according to claims 7 or 12 wherein the polyol-impregnated SiO₂ is impregnated with wax before adjusting particle size distribution.
14. Process according to claim 7 wherein a suspension of SiO₂, wax emulsion and polyol is spray-dried.
40. 15. Process according to claims 6 or 7 wherein the SiO₂ is already impregnated with polyol during washing by adding the polyol to the wash water.
16. Process according to claims 6 or 7 wherein the SiO₂ is already impregnated with polyol in the hydrogel state by adding the polyol to the liquid phase surrounding the hydrogel, or in the hydrosol state by adding the polyol to the water glass or to the diluted sulphuric acid during the precipitation of the SiO₂.
45. 17. Use of the SiO₂-flattening agent as in one of claims 1 to 5, or as produced according to the process in one of claims 6 to 16, for the preparation of thixotropic and non-thixotropic paints and lacquers.
18. Use according to claim 17 wherein the thixotropic paints and lacquers are based on polyamide-modified alkyd resins.
50. 19. Use according to claims 17 or 18 wherein SiO₂ or wax-impregnated SiO₂ and polyol are introduced into the paint or the lacquer as separate components, or SiO₂ or wax-impregnated SiO₂ and polyol are brought together first, and then the resulting product is incorporated into the paint or the lacquer.



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Patentamt

EUROPÄISCHER RECHERCHENBERICHT

Nummer der Anmeldung

EP 91101257.3

EINSCHLÄGIGE DOKUMENTE			
Kategorie	Kennzeichnung des Dokuments mit Angabe, soweit erforderlich, der maßgeblichen Teile	Betrifft Anspruch	KLASSIFIKATION DER ANMELDUNG (Int Cl.)
X	<u>GB - A - 1 395 700</u> (LAPORTE INDUSTRIES LIMITED) * Claims 1,4; page 2, lines 16-30; page 3, lines 7-24, 106-130; page 4, lines 1-12, 27-31 *	1-10, 17	C 09 C 1/30 C 09 D 5/04 C 09 D 167/00 C 09 D 7/02
X	<u>US - A - 4 173 491</u> (ABRAMS et al.) * Claims; column 3, lines 35-44; column 4, lines 62-64; column 5, lines 22-24 *	1,3,5, 6,8, 17	
X	<u>US - A - 3 436 241</u> (DURRANT) * Abstract; column 1, line 23 - column 2, line 64	1,3,5, 6,8, 10,12, *17,19	
X	<u>CH - A - 362 059</u> (DEUTSCHE GOLD- UND SILBER-SCHNEIDEANSTALT) * Claims; page 1, line 64-74; page 2, lines 60-72 *	1,5,6, 10,17	RECHERCHIERTE SACHGEBIETE (Int Cl.) C 09 C C 09 D
Der vorliegende Recherchenbericht wurde für alle Patentansprüche erstellt.			
Recherchenort WIEN		Abschlußdatum der Recherche 13-05-1991	Prüfer HAUSWIRTH
KATEGORIE DER GENANNTEN DOKUMENTEN			
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